Chapter 1

INTRODUCTION

People who recognize that our modern life style is dependent, to a large extent, on the use of organic polymers as thermal and electrical insulators, may be amazed to learn that specific plastics may also be used as conductors of electricity. In addition to representing the kind of polymers, this use as conductors will lead to developments which were not possible with other accessible materials of construction [1].

In the modern era, plastic and electrical devices are always strongly integrated together. In the year 1977 an electrically conductive, quasi one-dimensional organic polymer, polyacetylene was discovered [2] and during the past twenty years, a variety of diverse conducting polymers have been developed [3]. These Polymers have numerous attractive properties as compared to inorganic materials. They are light weight, low-priced, breakage tolerant, flexible, and easily processed and fabricated. They can be shaped into the complex structures and their properties can be altered according to demand [4]. With the rapid use of materials in science and technology, a variety of materials with intelligence embedded at the molecular level are developing rapidly. These intelligent materials can sense discrepancies in the environment, process the information, and take action accordingly. Excitement about these polymeric materials is evidenced by the fact that the field of conducting polymers has attracted scientists from different areas of interest such as synthetic chemistry, electrochemistry, solid state physics, materials science, polymer science, electronics and electrical engineering. Some of these polymers show shape memory behaviour and are known as Electro active polymers (EAP). The Carbon nano-tubes (CNT) on other hand have unique properties and expected to change or modify the characteristic properties of EAP. Thus, we can improve particular properties of host polymer (EAP) by inclusion of CNT. This forms the basis of our thesis. The brief reviews of our research work based on CNT doped EAP are given in following section.
1.1 Electro active Polymer (EAP)

Polymers that respond to external stimuli by altering shape or size have been known well and studied for more than a few decades. They respond to stimuli such as an electric field, a magnetic field and light [4]. These intelligent polymers can collectively called active polymers. There are many kinds of active polymers with different controllable properties, because of a variety of stimuli. They can produce permanent or reversible response and can be passive or active by embedment in polymers, making them smart in structures.

The field of EAP emerged back in the year 1880, when W. Roentgen designed an experiment in which he examined the effect of an electric current on the mechanical properties of rubber. But with passage of time, there has been a fast growing interest in electro active polymers, because these exhibits a change in shape or size when stimulated by an electric field. These EAP undergoes a large amount of deformation while sustain with large forces. Therefore, this typical phenomenon leads the material to easily manufacture into different shapes due to the ease in processing many polymeric materials, which makes them extremely versatile materials. The most common applications of EAP are in biosensor, artificial muscles, actuator and gas sensor etc. [5]. EAP materials can potentially be joined together into microelectronic-mechanical system (MEMS) to produce smart actuators.

Electro active polymers have emerged with enormous potential enabling the improvement of unique biomimetic devices. As synthetic muscles, EAP actuator offer capabilities that are currently considered science fiction. For growing such actuators required development on all fronts of the field infrastructure. Enhancement of the performance of these EAP will require advancement in related computational chemistry models, comprehensive material science, electro-mechanics analytical tools as well as improved material processing techniques. These developments enable biologically inspired robotics and use effective EAP actuators to mimic nature would vastly expand the collection and functionality of robots which are currently available. The making of robots that are actuated by EAP as artificial muscles are controlled by artificial intelligence would create new approaches in science and technology. Such types of capabilities are expected
to change future robots, significant research and development effort. It is needed to develop robust and effective EAP-based actuators.

Electro-active polymers (EAP) are new materials of actuator technology which are light in weight and can respond to an electric field to exhibit large displacement. EAP have great ability to imitate the properties of natural muscle especially the energy density and displacement. Today, there is more and more number of EAP material and technologies have been activated and developed.

![Image](image_url)

Figure 1.1: Grand challenge for the development of EAPs actuated robotics [4].

### 1.1.1 Type of Electro active Polymers

These EAP are mainly categorized into two different types depending on the mechanism responsible for actuation, as electronic EAP (which are driven by electric field or coulomb forces) and Ionic EAP (which change shape by mobility or diffusion of ions and their conjugated substances) [5-6].

Table 1.1 Broad classifications of EAP.

<table>
<thead>
<tr>
<th>Field Activated</th>
<th>Ion Activated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ferroelectric Polymer</td>
<td>1. Ionic Polymer-metal Composites</td>
</tr>
<tr>
<td>2. Polymer electrets</td>
<td>2. Ionic gels</td>
</tr>
<tr>
<td>3. Dielectric Elastomers</td>
<td>3. Conducting Polymer</td>
</tr>
<tr>
<td>4. Electrostrictive polymer</td>
<td>4. Electrorheological Fluid</td>
</tr>
<tr>
<td>5. Liquid Crystal Elastomer</td>
<td>5. Carbon Nanotubes</td>
</tr>
<tr>
<td>6. Electrostrictive Graft polymer</td>
<td></td>
</tr>
</tbody>
</table>
From Literature survey, it can be found that a lot of work has been done on such
types of materials by different research groups. But research is still going on because of the
importance of these materials. Integrated by the analysis of literature review, we
concentrated our study on Liquid Crystal Elastomer (Field Activated) and conducting
polymer (Ion activated). These two Electro-active Polymers are explained below in detail:

1.2 **Field Activated Polymer**

1.2.1 *Liquid Crystal Elastomer (LCE)*

Liquid crystals are unusual materials, that can flow but the spatial variation of the average
molecular orientation direction is resisted by frank elasticity. Polymers too are unusual as
they can show elasticity. Liquid crystals Polymers exhibit unique effects that are not
simply the enhancement of the liquid crystals or polymers separately. Polymer liquid
crystal, polymer chains with rigid anisotropic units, can order in a particular manner. These
molecules expand when these component rods orient. A change of shape thus takes place,
the effect however is very less. Linking the polymer chains together into a gel network
fixes their topology and the melt becomes an elastic solid-a rubber [7]. These materials are
known as liquid crystals elastomers (LCE). In simple elastomers entropy change of
polymers chains on relative movement of their cross-linked end points results in the elastic
response. In LCE orientational order can be induced within these chains and its director
rotate independently of deformation of the cross-linking points resulting in shape change.
This is known as the Cosserat medium and one expects unique physical properties in it,
especially for large deformations. Liquid crystal elastomers bring together three important
ideas: orientational order in amorphous soft materials, responsive molecular shape and
quenched topological constraints which helps to create many new physical phenomenons
like extreme opto-mechanical effects, rotator mechanical coupling etc [8-12]. Liquid-
crystalline elastomers are placed in a separate category from any other material on basis of
physical properties.

Firstly, concept of these LCE was put forward by the P.G Gennes in 1975 [13].
However, the first side-chain LCE was synthesized by Finkelmann *et al.* in 1981 [14]. For
variety of LCE, Ringsdorf and Finkelmann [15-17] used polyacrylate backbones with a
number of mesogenic pendants. These polyacrylate-based polymer chains have certain
practical disadvantages like high glass transition temperature, low backbone anisotropy etc. However, polymers based on siloxane backbones show much higher chain anisotropy and are conveniently liquid crystalline at room temperature. The Cornell group has produced lightly cross-linked (i.e. rubbery without swelling) Nematic and smectic elastomers based on the rod-like mesogenic monomers connected via flexible spacers [18-19]. Another group of Nematic main-chain elastomers based on semi-flexible polyether chains have been prepared by Finkelmann and co-workers [20]. Lyotropic LCE system has also been synthesized in Freiburg [21].

Initially research was mainly focused on synthesis and some characterization work of LCE. In recent years, the emphasis is being given on to studies of new physical properties and the area of research into liquid-crystalline elastomers has been significantly broadened. Various researchers have studied the physical properties of these materials due to the growing ability of the research group to synthesize LCE. Finkelmann et al. (1981) measured visco-elastic and opto-elastic properties as well as LCE behaviours in electric field [14]. Tajbakhsh et al. (2001) report systematic study of uniaxial monodomain nematic elastomers. They found that results are sensitive function of concentration of main chain component [22]. Terentjev et al. (2001) studied a wide range of photo sensitive materials based on azobenzene molecular moieties. They found that differing composition & topologies are reflected in varied mechanical response to radiations with ultraviolet light [23]. Finkelmann et al. (2002) studied mechanical properties of monodomain side chain nematic elastomers. They found that relaxation time is slowest relaxation time of network (as whole) and are consistent with hydrodynamics description of Nematic elastomers [24]. Dannio et al. (2008) studied thermo-tropic and elastic properties of main chain LCE by monomers and cross-linker molecular control. They found that choice of cross linker can be made according to behaviour expected for materials [25]. In one way or other many new physical properties of these materials have been discovered. Theories have been formulated to describe the nature and properties associated with these materials. The main features of Cosserat-like rubber elasticity can be explained using the limit of continuum linear theory [26]. This is fully applicable to a number of physical effects naturally involving small deformations e.g. acoustic waves or thermal fluctuations. The orientational ordering properties of LC systems and the rubbery elasticity of polymer networks (Warner &
Terentjev 2003) can be divided into two categories, depending on the LC phases exhibited by the systems, namely Nematic (Finkelmann et al.) and Smectic LC elastomers (Lehmann et al.). The spontaneous shape change and soft elasticity are two key phenomena in LCE that determine their physical responses and their potential for application in actuators [27]. The actuation mechanism is different for different type of LC elastomers. These phases and their application in actuators are discussed in detail in following sections.

1.2.2 Nematic LCE

The Nematic phase is simplest phase. Long polymer chains, with incorporated mesogenic units can order nematically and form liquid crystal polymers. The rod character of molecules just changes little when they orient to form a Nematic phase. These molecules start elongate when their component rods orient. So there is a change of average molecular shape from spherical to spheroidal as the isotropic polymers becomes Nematic as shown in Figure 1.1. Nematic elastomers typically elongate spontaneously in the presence of Nematic (orientational) order, and reversibly contract when the order is lost (typically by heating). Nematic order can also be re-directed by electric fields or by boundary conditions and change the macroscopic shape. This change can be at low energy, so the phenomenon is called "soft elasticity" [7]. Theoretically predicted effect of soft elasticity, a remarkable phenomenon when there is no rubber-elastic energy (without any energy loss) in response to certain sets of strains, has been confirmed by several experimental findings. It is a large amplitude effect though there is a small threshold to director response. Director rotation proceeds and concludes in a singular manner during the low energy deformation.

At the N-I transition temperature; there is a spontaneous shape change of the liquid crystal elastomers due to change of rotation of the liquid crystalline side chains. This shape change occurs nearly at a constant volume i.e. the molecule expands in one direction and contracts from other. This gives a flexing effect when the material is pinned on the substrate. This dramatic effect offers a door to use this material in artificial muscles/MEMS/MOEMS. It is a very recent field of research and very-very few research groups are seemed to work over this topic.

Such LCE type materials exhibit very rich elastic behaviour as they couple elastic fields and mobile liquid crystal order. The liquid crystallinity of these solid LC allows
these to shape change without any energy cost. These promising results indicate that LCE materials will certainly play an important role in the development of functional materials. But main issues that need to be examined various properties like stress-strain behaviour, thermo elastic (mechanical properties), optical, ferroelectric, electrooptic and dielectric properties etc. of these materials.

Figure 1.2: Change of average molecular shape from spherical to spheroidal [7].

However, due to very few researches on this material only two or three type properties are studied till now and none of group have studied dielectric properties. The properties of soft elasticity and large spontaneous shape change, suitability of these materials for application in generic large scale actuators/sensors [28-30] and in biology like for the formation of artificial Muscles/MEMS/MOEMS have made liquid crystalline elastomers an area of fundamental interest for Physics and Biophysics in micro-gravity. The probability is therefore large that qualitatively new directions as well as novel application potential in physics and biophysics could emerge.

1.3 Ion Activated Polymer

1.3.1 Conducting Polymer (CP)

In the past, it was considered that organic polymers are excellent insulators which provide significant advantages in support of various applications [31]. However, this idea was initially challenged when reports of conducting or semiconducting polymeric materials for instance polyacetylene and polyaniline began to appear in the literature [32]. It was only
when the doping of polyacetylene had succeeded that new concepts began to be realized and a new category of organic polymers *i.e.* conducting polymers, with the extraordinary ability to conduct electrical current began to support marvellous scientific and technological interest. In semiconductor physics undoped semiconductors are intrinsically conducting, whereas the doped semiconductors are extrinsically conducting. On the contrary, doped polymers are often referred to as “intrinsically conducting polymers”. It differentiates them from polymers which attain conductivity by loading with conducting particles such carbon black, fibers of stainless steel or metal flakes.

The intrinsically conducting polymers (ICPs), usually known as “synthetic metals”, refer to the category of organic polymers which possess not only the mechanical properties and procedure of conventional polymers, but also show inimitable electrical, electronic, magnetic and optical properties of the metals, which conventional polymers do not possess [33]. The distinctive property of this category of polymers is the intrinsic ability of the conjugated polymer backbone to sustain electrical conduction. Thus, electrical conductivity is accomplished by the charge carriers *i.e.* electron or hole, through a π conjugated polymer backbone.

Since the early discovery in 1977 by Alan G. MacDiarmid and his co-workers [32], that polyacetylene, \((\text{CH})_x\), *viz.* usually known as the prototype conducting polymer, could be either chemically or electrochemically (p- or n-doped), to behave as a conductor and the development of the conducting polymer field has continued to accelerate with an unpredictably rapid rate. This rapid growth rate has been stimulated not only by fundamental synthetic novelty of the field and significance to a cross-disciplinary section of investigators *i.e.* chemists, electrochemists as well as experimental and theoretical physicists and electronic/electrical engineers, but to its genuine and potential technological applications.

There are so many various kinds of polymers which undergoes redox doping process other than cis and trans polyacetylene, \((\text{CH})_x\) [34]. It has been found that polymers e.g. polyparaphenylene, poly (phenylenevinylene), polypyrrole, polythiophene, polyfuran etc. [35-39], and their derivatives (ring- and N-substituted) as shown in Figure 1.3 can also undergo redox p-doping and/or dedoping. Moreover, the synthesis of new polymer systems such as poly(heterocyclevinlenes), where \(Y=\text{NH}, \text{NR}, \text{S and O}\), also have attracted
considerable curiosity because of their exceptional physical properties combinations, solution processibility and environmental stability in doped form [40].

Conducting polymers are new category of materials which exhibit reversible redox behaviour and the odd combination of properties of metal and plastics. Conducting polymers has been observed as frontier area of major research and prospective materials for technological applications since last ten years [41-43]. These polymers are electronically conducting organic materials. These materials are actuated when the electronically changing oxidation state i.e. positively charged leads to the flux of ions into or out of the polymer backbone which cause deformation. Solvent flux may also occur when there is a difference in the ion composition. The addition and removal of ions between polymer chains is taken as the primary factor for dimensional change, where as the conformational change and solvent flux are considered as the secondary factors [44-45]. The polymerization mechanism, processability and the transport mechanism [46-48] are the point of interest in area of academic and scientific attractions. This class of conducting polymers belonging to polyenes or polyaromatic such as polyaniline, polythiophene, polypyrole, polyparaphenylene, polyacetyline has been studied extensively.

Figure 1.3: Chemical structure formula for some selected intrinsically conducting polymers [4].
1.3.2 Polyaniline (PANI)

In 1835, Polyaniline was firstly identified as “aniline black”, a term used for any product obtained by the oxidation of aniline. A few years later, the tentative analysis of the products carried out by the chemical oxidation of this aromatic amine [49]. Subsequent investigators [50-51] have verified these results and similar observations have been prepared during the oxidation of aqueous hydrochloride acid solutions of aniline. The polyaniline most likely earliest known synthetic polymer [52-54], refers to a large class of conducting polymers which have general formula in Figure. 1.4. A large variety of derivatives can be prepared through substitution in the ring or on the N atoms. One of the special properties of polyaniline is that it can be doped by protons. Thus, the properties of the doped polymer can be turned by incorporating different dopant anions.

![Figure 1.4: Polyaniline general formula [50].](image)

It has been found that polyaniline can exist in three different, isolable oxidation states at molecular level [55]. They are leucoemeraldine oxidation state, the emeraldine oxidation state and pernigraniline oxidation state. Other oxidation states are also the consequence of physical mixture of these oxidation states.

(i) Leucoemeraldine base: the fully reduced form of non-doped polyaniline. It is composed exclusively of reduced units as shown below:

![Figure 1.5: Leucoemeraldine Base [55].](image)

(ii) Pernigraniline base: the fully oxidized form of non-doped polyaniline. It is composed solely of oxidized base unites as represent below:
(iii) Emeraldine base: the intermediate oxidation state of polyaniline. It is composed of equal amounts of alternating reduced base and oxidized base units as represent below:

![Figure 1.6: Pernigraniline Base [55].](image1)

![Figure 1.7: Emeraldine Base [55].](image2)

Among all the above different forms of Polyaniline (PANI), Emeraldine base is extensively studied and much worldwide interesting polymer for the reason that of its high electrical conductivity, oxidative properties, environmental stability and ease of preparation etc. In 1862, it was first prepared by Letheby via anodic oxidation of aniline in sulphuric acid [52].

One of the surprising quotations about PANI given by Prof. A.G. MacDiarmid tha “there are as many different types of PANI as there are people who synthesized it” [32] has been a wide source of motivation. This statement elaborate the different properties of polyaniline such as optical and electronic, thermal and environmental stability changes with method and condition in which has it been synthesized. Therefore, the way of synthesis decides the conductivity, band gap, chemical structure, polymerization mechanism, ease of attachment and detachment of different functional groups.

These conducting polymers may exist in variety forms which differ in chemical as well as physical properties. Polyaniline exist in numerous oxidation states with electrical conductivity varying gradually from 1-10 S/cm. However, only one form, called emeraldine salt is electrically conducting. These conducting polymers can be synthesized
easily by electrochemical or chemical oxidation of aniline in aqueous acidic media using common oxidants likely ammonium peroxidisulphate. Therefore, these conducting polymers polyaniline [PANI] has rapidly become the subject of considerable interest for physicists, chemists and material scientists.

1.3.3 Method of Synthesis

As discuss in above section, polyaniline can be chemically or electrochemically synthesized via the oxidative polymerization of aniline monomer in the presence of aqueous acid e.g., 1M HCl solution [57]. The synthesized polymer is well known an emeraldine salt. For chemical synthesis, there are many different oxidizing agents, including: ammonium peroxysulfate, hydrogen peroxide, ferric chloride and ceric nitrate and sulfate [58-62]. Normally the ratio of oxidizing species to aniline has also been reported to be oxidant/aniline 1.25 (a stoichiometric equivalent of oxidant) [63-64]. Other chemical polymerizations incorporate a stoichiometric deficiency of the oxidant with respect to aniline (oxidant/aniline ratio 0.25) [65].

Polyaniline can also be synthesized electrochemically by oxidation of aniline on an inert metallic like platinum (Pt) electrode or on a piece of conducting Indium Tin Oxide (ITO) glass slides [66-69]. The electrochemical polymerization of aniline can be carried out in acidic media via applying constant potential, constant current and by repeatedly cycling the applied voltage between two pre-selected potentials. These polymerization methods recommend the possibility of conveniently investigates various chemical and physical properties of polyaniline by using FTIR and UV-Vis spectroscopic techniques.

1.3.4 Polymerization Mechanism

The synthesis of polyaniline does not matter whether synthesized electrochemically or chemically because it is commonly assumed that there is a close similarity in their polymerization mechanism. In both case, the polymerization process proceeds via the following mechanism:

The first step is the formation of the radical cation by an electron transfer from the 2s energy level of the aniline nitrogen atom, as shown in Figure 1.8.
The formed aniline radical cation has different resonant forms in which structure (c) is more reactive because of its essential substituent inductive effect and absence of steric hindrance. Further, next step correspond to the dimer formation so-called “head-to tail” reaction between radical cation and its resonant form (most probably form (c)) in acidic medium. Then dimer is oxidized to form a new radical cation dimer, as shown in Figure 1.9.

Next, the formed radical can react either with the radical cation monomer or with the radical cation dimer to form a trimer or tetramer respectively. If this continues, similar to the above steps, the polyaniline (PANI) polymer is finally formed as shown in Figure 1.10.
Finally, it is mentioned that besides idealized formation of p-coupled PANI chains in the reactions described above, some side reactions were also identified:

(i) The coupling of aniline with its oligomers in “ortho” position
(ii) The development of benzidine groups (“tail to tail” coupling)
(iii) The substitution of chlorine in aromatic ring likely in systems with HCl, LiCl or NaCl
(iv) The formation of azo groups like N=N bonds
(v) The formation of N-CAr grafting bridges between chains;
(vi) Polymer hydrolysis (=O and -OH groups).

Figure 1.10: Possible approach of PANI polymer formation.

Conducting polymers are replacing natural and inorganic materials in application requiring excellent physical properties like mechanical one and lightweight. The mechanical properties of polymers can be tailored to provide strong materials with high toughness and low resistance. Polymers are insulators type materials due to covalently bonded polymer chain in atoms. But it is found that conductivity of polymers can be made to vary over a very wide range, starting from insulating to semiconductor and towards metallic, by varying the concentration of different dopant.

Electro-active polymers have been investigated and applied in many different fields especially in biological muscle, because their properties allow them to perform efficiently
as human muscle. One of the advantage of EAP is that they can be easily formed in various shape and allow them to develop as a smart actuators. More and more industries are benefiting from the enhancement of this technology [4].

Since the need of our society about these smart materials goes on increasing, more researches are ongoing to gain better understanding of the manufacturing techniques, electroding, shaping and handling of these materials. According to percolation theory, carbon nanotubes allow for the formation of a conductive network within EAP which increase intrinsic high conductivity. Thus, in order to improve these phenomena, EAP are doped with dopant carbon filler or nanoparticle etc. In our research work, we use dopant as Carbon nanotube (CNT) and Zinc oxide (ZnO) nano-particles to improve properties, performance, efficiency and stability of EAP type smart materials. This study could not lead to development of improved EAP only, but it will also include to know how CNT and ZnO doped EAP composites behave and modified physical phenomenon. In following section, we discuss CNT in term of its structure, type, properties and synthesis processes.

1.4 Carbon Nano Tubes (CNT)

Since 1991, Sumio Iijima was discovered carbon nanotubes (CNT) [70]. The structure of CNT can be completely illustrated by considering the two ‘arche type’ CNTs which formed by cutting a fullerene (C60) molecule in half and placing a graphene cylinder between two halves. Dividing C60 along one of the fivefold axes, produces the ‘armchair’ nanotube as shown in Figure 1.14, while bisecting C60 parallel to one of the threefold axes results in the ‘zigzag’ nanotube shown in Figure 1.14 [71-72].

1.4.1 Structure of Carbon Nano Tube

The important studies of CNT structure have explored via using high-resolution microscopy technique. These experimental techniques have established that CNT tubes are cylindrical in structures based on the hexagonal lattice of carbon atoms which forms crystalline graphite. CNT are of three types called armchair, zigzag and chiral nanotubes depending on how the two-dimensional graphene sheet is “rolled up”[71]. These CNT are formed from pure carbon bonds have two covalent bonds: sp² and sp³. The former
constitutes graphite and the latter constitutes diamond. Figure 1.11 shows the structure of graphite and diamond.

The \( sp^2 \) hybridization, composed of one s-orbital and two p-orbitals, is a strong bond within a plane but weak between planes. When more bonds come together, they form sixfold structures, like honeycomb pattern, which is a plane structure, the same structure as graphite. Graphite is stacked layer by layer so it is only stable for one single sheet. Wrapping these layers into cylinders and joining the edges, a tube of graphite is formed, called nanotube.

![Figure 1.11: Structure of graphite and diamond.](image)

Atomic structure of nanotubes can be described in terms of tube chirality or helicity, which is defined via chiral vector, \( Ch \), and the chiral angle, \( \theta \). Figure 1.12 shows, visualized cutting a graphite sheet along the dotted lines and rolling the tube so that the tip of the chiral vector touches its tail. The chiral vector, often known as the roll-up vector can be described by the following equation: \( C_h = n a_1 + ma_2 \), where the integers \((n, m)\) are the number of steps along the ziz-zag carbon bonds of the hexagonal lattice, and \( a_1, a_2 \) are unit vectors in the two-dimensional hexagonal lattice, as shown in Figure 1.12.
Figure 1.12: Schematic diagram showing how graphite sheet is rolled to form CNT.

Figure 1.13: Atomic structure (a) an armchair and (b) a zig-zag nanotubes

Chiral angle determines the amount of “twist” in the tube. Two limiting cases arises, where the chiral angle is at 0° and 30°. These limiting cases are referred to as ziz-zag (0°) and armchair (30°), based on the geometry of the carbon bonds around the circumference of the nanotube. The difference in armchair and zig-zag nanotube structures is shown in
In terms of the roll-up vector, the ziz-zag nanotube is (n, 0) and the armchair nanotube is (n, n). The roll-up vector of the nanotube also defines the nanotube diameter since the inter-atomic spacing of the carbon atoms is known.

### 1.4.2 Single-walled nanotubes (SWNT)

Most of single-walled nanotubes (SWNT) have a diameter near to 1 nanometer with a tube length that can be many thousands of times longer. The structure of a SWNT can be conceptualized by covering a one-atom-thick layer of graphite called graphene into a seamless cylinder.

![Image of nanotubes with labels (n,m) = (5,5), (n,m) = (9,5), and (n,m) = (10,5).]

Figure 1.14: The first two of these, known as “armchair” (top) and “zig-zag” (middle) have a high degree of symmetry. The third class of nanotube is known as chiral (bottom).

The way that graphene sheet is wrapped is represented by a pair of indices (n,m) called the chiral vector. The integers ‘n’ and ‘m’ denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If m = 0, the nanotubes are called zigzag. If m = n, the nanotubes are called "armchair". The terms "armchair" and zig-zag refer to the arrangement of hexagons around the circumference otherwise, they are called chiral, meaning that it can exist in two mirror-related forms as shown in Figure 1.14.
SWNT are a very important type of carbon nanotube because they exhibit important electric properties which are not shared by the multi-walled carbon nanotube (MWNT) variant. SWNT are the probably candidate for miniaturizing electronics past, the micro electromechanical scale which is currently the basis of modern electronics. The most basic building block of these systems is the electric wire and SWNT can be excellent conductors [73]. One very useful application of SWNT is in the development of the first intramolecular field effect transistors (FET).

1.4.3 Multi-Walled Nanotubes (MWNT)

Multi-walled nanotubes (MWNT) consist of multiple layers of graphite rolled in on themselves to form a tube shape. There are two models which can be used to describe the structures of multi-walled nanotubes. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders, e.g. Single walled nanotube (SWNT) within a larger single-walled nanotube as shown in Figure 1.15.

According to Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.3 Å. The special place of double-walled Carbon Nanotubes (DWCNT)
must be emphasizing here because they unite very similar morphology and properties as compared to SWCNT, while improving their resistance to chemicals very significantly.

1.4.4 Comparision between SWCNT and MWCNT

Table 1.2: Comparision between SWCNT and MWCNT

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Single walled carbon nanotubes</th>
<th>Multi walled carbon nanotubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Single layer of graphene</td>
<td>Multiple layer of graphene</td>
</tr>
<tr>
<td>2.</td>
<td>Catalyst is required for synthesis</td>
<td>Without catalyst can be synthesis</td>
</tr>
<tr>
<td>3.</td>
<td>It has poor Purity</td>
<td>Purity is high</td>
</tr>
<tr>
<td>4.</td>
<td>Possibility of defect is more during functionalisation</td>
<td>Possibility of defect is less but it is difficult to improve if occurred</td>
</tr>
<tr>
<td>5.</td>
<td>Less accumulation in body</td>
<td>More accumulation in body</td>
</tr>
<tr>
<td>6.</td>
<td>Characteristion and evaluation is easy</td>
<td>It has very complex structure</td>
</tr>
<tr>
<td>7.</td>
<td>It can be easily twisted and are more flexible.</td>
<td>It cannot be easily twisted</td>
</tr>
<tr>
<td>8.</td>
<td>Bulk synthesis is difficult because it requires proper control over growth and atmospheric condition.</td>
<td>Bulk synthesis is possible and easy</td>
</tr>
</tbody>
</table>

1.4.5 Why MWNT are preferred?

MWNT are less expensive than SWNT. MWNT are more chemical resistant than SWNT. Particularly, this is important when functionalization is required (this means embed of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In case of SWNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical as well as electrical properties. In case of double wall carbon nanotubes, only the outer wall is modified.
1.4.6 Properties of Carbon Nanotubes

CNT have gained an interest because nanoscale materials caused by their exceptional, outstanding properties such as: extremely high Young’s modulus, ultimate strength, high electric and thermal conductivity. Moreover, CNT provide a remarkable model of a 1-Dim. system. More details on the properties of carbon nanotubes are presented below.

1.4.6.1 Electronic Properties

Due to its special structure, CNT shows exceptional properties. One of the important properties of CNTs is that it can exhibit characteristics of a metal or a semiconductor. It is determined by chirality and diameter that carbon nanotube acts as metal or semiconductor. If n-m =3q, where q is an integer nanotube acts as a metal otherwise it acts as a semiconductor. All armchair nanotubes are metallic, as are one-third of all possible zig-zag nanotubes. The diameter, d, is simply the length of the chiral vector divided by π, and we find that [72]

\[ D_t = (\sqrt{3}/\pi)a_{c-c}(m^2+mn+n^2)^{1/2}, \]

Where \( a_{c-c} \) is the distance between neighbouring carbon atoms in the flat sheet. The chiral angle is given by:

\[ \Theta = \tan^{-1}(\sqrt{3}n/(2m+n)) \]

Here, \( \Theta \) is chiral angle which in turn depends on m and n are integer.

The geometry of the nanotubes determines band structures and thus the energy band gap. The energy band gap of semiconducting CNT highly depends on the nanotubes diameter and is given by:

\[ \text{Energy gap} = 2\gamma_0a_{c-c}/d \]

Where, \( \gamma_0 \) denotes the C-C tight binding overlap energy (2.45 eV), \( a_{c-c} \) the nearest neighbour C-C distance (~1.42 Å), and d is the diameter of a nanotubes.

Based on their structure, CNT can be divided in singlewalled CNT (SWNTs) and multiwalled CNT (MWNTS). In general, MWNTs are quite often found to be one dimensional conductors with a high electrical conductivity (even >103 S/cm). The metallic properties of the MWNTs are due to their multiple-shell structure consisting of tubes with
various electrical properties, where additional electronic coupling between shells takes place. Moreover, MWNTs are predicted to have ballistic electron transport at room temperature (it refers to conduction where Ohm’s law not suitable to apply because resistance is not dependent on the CNT’s length). The electrical current that could be passed through a MWNT corresponds to a current density in excess of 107 A/cm².

1.4.6.2 Chemical Properties

Chemical or physical modification of the surface of CNT, e.g. by the attachment of certain molecules or functional groups is a very important issue in order to overcome their poor solubility in solvents. This process is known as functionalization. Functionalized CNT are very attractive for chemical and biological applications because of their strong sensitivity to chemical or environmental interactions. This leads to a broad range of applications, e.g. as sensors. Covalent and non-covalent functionalization, doping, decoration with organic as well as inorganic species of the surface of CNT lead to direct changes of the properties of CNT such as optical, electrical, and mechanical [74].

1.4.6.3 Mechanical Properties

The structural properties of CNT with strong σ bonds between the carbon atoms give nanotubes a very high Young’s modulus and tensile strength. The strength of the carbon carbon bonds in-plane, along the cylinder axis, retains the structure exceptionally strong resistance to any failure. CNT also have very good elasto-mechanical properties. Both experimental and theoretical investigations show extraordinary mechanical properties of individual MWNTs with Young’s modulus being over 1 TPa and a tensile strength of 10 - 200 GPa, which is several hundred times more than that of steel, while they are only one sixth as heavy.

1.4.6.4 Other Properties

Besides the outstanding mechanical and electrical properties, CNT exhibit interesting thermal and optical properties. Defect-free nanotubes, especially SWNT, offer a direct band gap and a well defined band and sub-band structure, which is ideal for optical and
optoelectronic applications. The experimental measurements of the optical absorption of a bundle of single-walled CNT show that there are several groups of absorption peaks and each group is closely related to the nanotube geometry.

### 1.4.7 Synthesis of Carbon Nanotubes

Since carbon nanotubes started to attract the interest of the scientists and the industries, several methods of production of carbon nanotubes have been developed. These procedures can be divided in two categories: physical and chemical. The physical processes are based on the physical principles of carbon conversion into nanotubes. In this group have arc discharge method, which was one of the oldest methods, and the laser ablation which was first discovered in 1995 at Rice University [75]. The chemical processes are based on gas-phase techniques where the tubes are formed by decomposition of a carbon-containing gas and the main representative is the CVD method.

#### 1.4.7.1 Arc-Discharge method

The synthesis of CNT has been exclusively described by different workers [76]. The arc discharge technique was utilized by Iijima to produce new type of carbon structures in a way similar to the ones used for the production of fullerenes.

![Schematic representation of Arc-Discharge method](image)

Figure 1.16: Schematic representation of Arc-Discharge method [79].
The principle of the arc discharge method is based on the deposition of charged carbon vapor on a cathode electrode in the presence of a catalyst. The analytical process has been described in several publications and books [77-78]. By this method high quality nanotubes can be synthesized in high yield. The main drawbacks are that it is an expensive and complicated procedure [79]. A schematic representation of Arc-Discharge method is shown in Figure 1.16.

1.4.7.2 Laser Ablation Method (LAM)

The laser ablation process is also based on the formation of carbon vapour. For that reason laser power is used to strike at graphite in high temperature conditions. The nanotubes made by this method form bundles of 10-20 nm while their length is up to 100 μm. The diameter and the length of the nanotubes can be controlled by varying several parameters of the process [80]. A schematic representation of Laser ablation method is shown in Figure 1.17.

![Schematic representation of Laser ablation method (LAM)](image)

Figure 1.17: Schematic representation of Laser ablation method (LAM) [81].

The carbon nanotubes that are produced by this method are characterized as high quality, due to their perfect carbon structure and their excellent electrical and optical properties. However, the cost of this procedure is very high [81]. In general the physical processes suffer from three main drawbacks: the large amount of energy that is needed
(which increases also the cost), the difficulty of supplying large amounts of solid carbon/graphite for the large production of nanotubes and the purification process that is required for the removal of side products.

### 1.4.7.3 Chemical Vapor Deposition (CVD)

The chemical methods for the synthesis of CNTs are based on the chemical vapor deposition (CVD) technique. Two variations of this method were developed: the HiPco by Nikolaev [80], where high pressure was used and the CoMoCAT by Resasco [82] with the use of two catalysts (Co and Mo) in CO gases. The diameter of the nanotubes depends on the size of the catalyst particles on which the nanotubes are built on, while the deposition technique can affect the electrical properties of the tubes. A Schematic representation of Chemical vapor deposition is shown in Figure 1.18.

![Schematic representation of Chemical vapor deposition (CVD)](image)

**Figure 1.18: Schematic representation of Chemical vapor deposition (CVD) [82].**

Plasma assisted CVD has been developed for production of vertically grown carbon nanotubes. The CVD method is easy to apply, since the reaction reactor is common and the raw materials are readily available in the form of gases. In addition good yields of high quality CNT are produced with relatively low cost [83]. Of course there are lot of improvements that needed to made, especially in the purity and the price of the tubes, but
the CVD is currently the most promising solution.

The advantages and the drawbacks of both the physical and chemical procedures are summarized in detail. The comparisons of main characteristics for different processes involved in CNT synthesis are given below in tabular form in Table 1.3.

Table 1.3: Comparison of main characteristics for different processes of CNT synthesis.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Synthesis Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Arc-Discharge</td>
</tr>
<tr>
<td>Raw materials availability</td>
<td>Difficult</td>
</tr>
<tr>
<td>Energy requirement</td>
<td>High</td>
</tr>
<tr>
<td>Process</td>
<td>Difficult</td>
</tr>
<tr>
<td>Reactor design</td>
<td>Difficult</td>
</tr>
<tr>
<td>Purity of product/purification</td>
<td>High/require refining</td>
</tr>
<tr>
<td>Process nature/yield</td>
<td>Batch type/70%</td>
</tr>
<tr>
<td>Cost per unit</td>
<td>High</td>
</tr>
</tbody>
</table>

As a conclusion, we remark that the CVD method is the most promising for large production of CNT, but the price of the pure CNT remains high. The main issue of the nanotubes production concerns their impurities (amorphous carbon, catalysts) that remain in the product after the synthetic procedure. In addition, during the synthesis of CNT in large scale, the diameter and chirality of the nanotubes cannot be controlled. New synthetic and purification methods are required as CNT are becoming a necessary material for the organic electronics. The properties of CNT are closely related to their method of production. A recent processing technique, flame synthesis, is also currently being developed. In early work the arc discharge and laser vaporizations processes were the most
common forms of nanotubes production, typically resulting in nanotubes with low structural defects and thus excellent physical properties. In these techniques SWNT are typically formed in the presence of a metal catalyst, which seems to preclude the formation of MWNT. In the interest of developing a process that can be scaled-up for industrial production, a great deal of work has been devoted to techniques that may be classified as chemical vapor deposition (CVD). While CVD processes have been used to produce a wide variety of carbon structures, the major drawback of these methods is the reduced structural integrity of the nanotubes.

1.4.8 Potential Application of CNT

The unique structure of a CNT, different from graphite and conventional carbon has attracted many researchers from chemistry, physics and materials science. The CNTs are used in various applications like Atomic Force Microscope (AFM) probe tips [84], Electrodes for rechargeable batteries [85], Charge storage devices [86] Chemical and bio sensors [87] Actuators and artificial muscles [88] Hydrogen storage devices [89]. Supercapacitors [90-91].

1.5. Metal Oxide Nano-materials: Zinc Oxide (ZnO)

Metal oxide nano-materials constitute one of the most important classes of materials due to their non-toxic nature, high chemical and physical stability and biological properties etc. Among metal oxide nanomaterials, zinc oxide (ZnO), a II-VI semiconductor compound is a special material due to its unique properties and wide range of applications [92-98]. Most importantly, ZnO has been regarded as generally recognized as safe (GRAS) material by the U.S. Food and Drug Administration (21CFR182.8991) [99-100]. ZnO has large exciton binding energy (60 meV), high optical gain at room temperature, large saturation velocity and so on [101-104] Various methods such as a hydrothermal method, sol-gel, spray pyrolysis, and direct precipitation methods have been adopted for the fabrication of nanosized ZnO particles with a uniform morphology and size [105-109] The properties of ZnO at nanoscale level different from that of bulk ZnO materials. Nanoscaled ZnO possesses
higher surface-to-volume ratio and sufficient surface active sites for remarkable role in study of physical properties and application point of view.

1.5.1 Physical Properties of metal oxide Zinc Oxide (ZnO)

From literature survey, it is found that, depending upon the method of synthesis, ZnO form a very large variety of crystalline shapes, usually having hexagonal wurtzite structure in which each O\(^{2-}\) ion is surrounded by four Zn\(^{2+}\) at the corners of a tetrahedron with a typical sp\(^3\) covalent bonding and vice versa as shown in Figure 1.19. Such a tetrahedral and non-centro symmetric structure with polar symmetry along the hexagonal axis is responsible for the anisotropic crystal growth of ZnO and the outcome is versatile morphologies for ZnO nanostructures like nanotubes, nanospheres, nanorods, nanofibres, nanowires, nanobelts nanoflowers, nanomashrooms and nanocubes etc. [105].

![ZnO unit cell (Wurtzite structure) with ionic positions of Zn\(^{2+}\) and O\(^{2-}\) ions](image)

Figure 1.19: ZnO unit cell (Wurtzite structure) with ionic positions of Zn\(^{2+}\) and O\(^{2-}\) ions [105].

Lattice parameters, \(a = 0.32495\) nm and \(c = 0.52069\) nm, with ratio of \(c/a =1.602\) corresponds to P63mc space group. The values of lattice constants \(a\) and \(c\) are sensitive to the structural point defects arising due to the presence of vacancies and interstitial sites on
the surface of ZnO. These imperfections or defects control the mechanical, thermal, electrical and optical properties of ZnO nanomaterials. The presence of excess zinc atoms function as donor interstitials causing n-type conductivity [110].

Table-1.4: represents some of the common physical parameters pertaining to ZnO [110].

<table>
<thead>
<tr>
<th>Physical parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>81.37g mol⁻¹</td>
</tr>
<tr>
<td>Color</td>
<td>Pure microcrystalline zinc oxide is white</td>
</tr>
<tr>
<td></td>
<td>Single crystal zinc oxide is colorless</td>
</tr>
<tr>
<td>Bond length</td>
<td>1.977μm</td>
</tr>
<tr>
<td>Relative density</td>
<td>5.607 g cm⁻³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6 W cm⁻¹°C⁻¹</td>
</tr>
<tr>
<td>Minimum pressure at melting point</td>
<td>7.82 atm</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>&lt;10⁶ cm⁻³</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td><strong>Lattice constants (T = 300 K)</strong></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.32495 nm</td>
</tr>
<tr>
<td>C</td>
<td>0.52069 nm</td>
</tr>
<tr>
<td>c/a</td>
<td>1.602</td>
</tr>
<tr>
<td>Refractive Index for wurtzite</td>
<td>2.029</td>
</tr>
<tr>
<td>Heat Capacity: Cp (25°C)</td>
<td>9.62 cal/deg/mol</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>4 x 10⁻⁶ /°C</td>
</tr>
<tr>
<td>Band gap</td>
<td>3.37eV (direct)</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
</tbody>
</table>

For nanosized ZnO materials, due to large surface area, the concentration of zinc/oxygen atoms residing on the surface is also greatly affected. The physical properties ZnO of semiconductor materials depend upon intrinsic as well extrinsic effects. Intrinsic effects arise due to the transition of the electrons between the conduction band and holes in the
valence band. On the other hand, extrinsic effects are related to dopant nature and concentration which create discrete electronic states and influence the optical absorption [111].

1.5.2 Why Nano-particles?

Nano-particles exhibit size related properties that differ significantly from those observed in micro-sized particles or bulk materials. Nano-particles can be embedded into different type of EAP like Polyamide, polyethylene, nylon, polyaniline etc. Among these polymers, nano-composite based on polyaniline is interesting and flexible. These nano-composites exhibit enhancements in different properties mainly due to high surface area to volume ratios, when homogeneous dispersion is achieved. Thus, nano-particles composed EAP shows enhancement in optical, electrical, magnetic and dielectric properties as compare to microparticles reinforced EAP.

1.5.3 Application of ZnO (Nanascale)

Semiconductor metal oxide nanomaterials have attracted a wide attention due to their various properties and wide applications. Among various metal oxide nanomaterials, the II–VI metal oxide zinc oxide (ZnO) possesses a special place due to its excellent properties such as wide band gap and high-exciton binding energy (60meV), biocompatibility, piezoelectricity etc. and extensive applications.

ZnO is a smart material with various applications, to name a few, ultraviolet (UV) lasers, light emitting diodes, photo-detectors, solar cells, chemical and biosensor piezoelectric transducers and actuators, hydrogen storage, photocatalysis, and so on [112-118]. A significant progress in this field has been made by integrating the unique properties of the EAPs i.e polyaniline with those of various metal oxide nanoparticles in the last few decade [119-120]. Conductive polymer nanocomposites (PNCs) find their technological applications and we got motivated to make composite of PANI and ZnO, believed to get novel properties resulting from the molecular level interaction of these two dissimilar chemical components [121].
1.6 Electro active Polymer Composites

Nowadays polymers play a very important role in numerous fields of everyday life due to their advantages over conventional materials such as lightness, low-cost production, and ease of processing. Altering and enhancement of the polymers’ properties occur, for example, through doping with various fillers such as metals, semiconductors, organic and inorganic particles and fibers, as well as carbon structures and ceramics; thereby enabling polymers to be used as a structural unit. Different dopant are used in polymers due to various reasons like improved processing, density control, optical effects, thermal conductivity, and control of thermal expansion, electrical properties, magnetic properties, flame resistance and improved mechanical properties such as hardness and elasticity.

1.6.1 CNT doped Polymer Composites

In 1999, CNT doped PANI composites were firstly synthesized [122] and since then it become the subject of intensive research and considerable progress has been made in their synthesis. For examples, PANI/MWNT composites synthesized by the chemical oxidation of aniline in acidic aqueous environments with an oxidizing agent such as ammonium persulfate to facilitate site-selective interactions between the quinoid ring of the repeating units of PANI emeraldine salt and MWNT [123], a coaxial nanowire of a PANI/MWNT composite prepared by electrochemical oxidation of aniline on a CNT electrode [124] and a PANI/MWNT composites with high electrocatalytic activity for formic acid oxidation, synthesized by microemulsion polymerization of aniline in the presence of CNT [125-126].

In 2003, the first attempt to synthesis of PANI/SWNT composites was done [127]. In case of SWNT, different compounds are obtained depending on the synthesis route and reactive agents which are used. Thus, in case of the chemical polymerization of aniline in the presence of SWNT, PANI doped with CNT fragments are obtained as a result of the breaking of the SWNT into small fragments when the oxidizing agent is K₂Cr₂O₇ and H₂SO₄. This experimental fact has explained by considering that the polymerization of aniline is controlled by the relationship between the monomer and the oxidizing agent defined by the K parameter [128], \( K = \frac{2.5n_{an}}{n_{oxne}} \), in which \( n_{an} \) and \( n_{ox} \) are the number of moles of aniline and oxidizing agent, respectively; \( n_e \) is the number of electrons.
necessary to oxidize one molecule of aniline to polyemeraldine. By decreasing the value of K parameter, one increases the yield of polymerization reaction [129] and this can be attained either by increasing the concentration of the oxidizing agent in relation to the monomer concentration or by reducing the aniline concentration with regard to the concentration of oxidizing agent.

The extraordinary properties of carbon nanotubes put together them very promising and favorable as fillers for production of a new class of polymeric heterostructures. In CNT-polymer composites, the nanotube-polymer interface enhance via chemical functionalization. The functionalized nanotubes are typically to disperse in organic solvents and water by easier way which can develop the dispersion and homogeneity of the CNT within the polymer. Although improvements in property based on carboxylated functionalized MWCNT in a polymer and SWCNT in epoxy have been obtained, results for amino (-NH₂) functionalized CNT composites have yet to be reported. In one study, amino-terminated MWCNT/epoxy showed improved dispersion which increases the interfacial interaction between nanotubes and polymer but no quantitative thermo-mechanical or chemical results are provided [130-132].

1.6.2 Dispersion of Carbon Nanotubes into EAP

The carbon nanotubes have strong van der Waals forces of attraction which tend to aggregate together inside the solution and form ropes, usually with highly entangled network structures. That’s why it is difficult to disperse CNT inside the polymers. But by careful procedure we can mix these two components without severe aggregation of nanotubes. The attractive forces also arise due to an entropic effect inside the polymer matrix [133]. Polymer chains in the region of the colloidal filler suffer an entropic penalty since roughly half of their configurations are precluded. Therefore, there is a depletion of the polymer in this region, resulting in an osmotic pressure forcing the filler particles to come together [134-137]. There are different methods by which CNT doped EAP composites can be synthesized, depending on the desired applications. The most important are:
1.6.2.1 Solution processing of composites:

The most common method based on the mixing of the CNT and a polymer in a suitable solvent before evaporating the solvent to form a composite film. The dispersion of components in a solvent, mixing, and evaporation are often supported by mechanical agitation (e.g. ultrasonication, magnetic stirring, shear mixing) [138-140].

1.6.2.2 Melt processing of bulk composites

This method concerns polymers that are insoluble in any solvent, like thermoplastic polymers [141-142]. It involves the melting of the polymers to form viscous liquids to which the CNT can be added and mixed.

1.6.2.3 Melt processing of polymer composite

CNT are added to the melts of the polymers. The formation of CNT doped polymer composites from their melts occurs through e.g. the melt- spinning process [143].

1.6.2.4 Composites based on thermosets

A thermoset polymer is one that does not melt when heated, such as epoxy resins. The composite is formed from a monomer (usually liquid) and CNT, the mixture which is cured with crosslinking/catalyzing agents [144-145].

1.6.2.5 Layer-by-layer assembly (LBL)

CNT and polyelectrolytes are used to form a highly homogeneous composite, with a good dispersion, good interpenetration, and a high concentration of CNT. This method involves alternating adsorptions of a monolayer of components which are attracted to each other by electrostatic interactions resulting in a uniform growth of the films [146].

1.6.2.6 In-situ polymerization

The polymer macromolecules are directly grafted onto the walls of carbon nanotubes. This technique is often used for insoluble and thermally unstable polymers which cannot be
melt processed. Polymerization occurs directly on the surface of CNT [139, 147]. In general, all of these different techniques give various results in terms of the efficiency of the nanotubes dispersion, interfacial interaction between components, properties of the composites and possible promising applications.

Among above discussed method, the most widely accepted methods are chemical oxidative polymerization method and electrochemical methods. Chemical oxidative method is preferred over electrochemical polymerization because of its cost effectiveness and bulk quantity of the polymer that can be prepared during the onset of a reaction.

1.7 Overview of Research Work

Our research work is based on synthesis and the physical properties of CNT doped EAP. Among EAP, we choose one electronic type EAP i.e liquid crystal elastomer synthesized by using Finkelmann procedure and other is ionic type EAP i.e polyaniline conducting polymer synthesized by using oxidative chemical polymerization procedure. Then, these synthesized EAP polymers are incorporated or dispersed with Multi Wall Carbon Nanotubes (also dispersion of zinc oxide nano-particle as additional work) to study the following important points:

(i) To synthesized Electroactive polymers both type electronic as well as ionic type.
(ii) The effect of multi wall carbon nanotubes on synthesized polymers on the molecular weight, crystallinity, conductivity and morphology of the polymer
(iii) The effect of filler (MWCNT) incorporation on DC conductivity of the resulting polymer composites.
(iv) To study the thermal, mechanical and morphological properties of MWCNT doped EAP.
(v) To explore the possible applications of the Electronic EAP and Ionic EAP, especially in the field of actuators.

The major part of motivation of our research work is to understand the synthesis procedure and measure the different physical properties of CNT doped EAP polymer nanocomposites. In addition to this, mechanical property of electronic type EAP i.e Liquid crystal elastomers (LCE) materials are also measured and discussed in detail.
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